Quantum Monte Carlo method using phase-free random walks with Slater determinants

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We develop a quantum Monte Carlo method for many fermions that allows the use of *any* one-particle basis. It projects out the ground state by random walks in the space of Slater determinants. An approximate approach is formulated to control the phase problem with a trial wave function $|\Psi_T\rangle$. Using plane-wave basis and non-local pseudopotentials, we apply the method to Si atom, dimer, and 2, 16, 54 atom (216 electrons) bulk supercells. Single Slater determinant wave functions from density functional theory calculations were used as $|\Psi_T\rangle$ with no additional optimization. The calculated binding energy of Si_2 and cohesive energy of bulk Si are in excellent agreement with experiments and are comparable to the best existing theoretical results.

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Quantum Monte Carlo (QMC) methods based on auxiliary fields (AF) are used in areas spanning condensed matter physics, nuclear physics, and quantum chemistry. These methods [1, 2] allow essentially exact calculations of ground-state and finite-temperature equilibrium properties of interacting many fermion systems. The required CPU time scales in principle as a power law with system size, and the methods have been applied to study a variety of problems including the Hubbard model, nuclear shell models, and molecular electronic structure. The central idea of these methods is to write the imaginary-time propagator of a many-body system with two-body interactions in terms of propagators for independent particles interacting with external auxiliary fields. The independent particle problems are solved for configurations of the AF and averaging over different AF configurations is then performed by Monte Carlo (MC) techniques.

QMC methods with auxiliary fields have several appealing features. For example, they allow one to choose *any* one-particle basis suitable for the problem, and to fully take advantage of well-established techniques to treat independent particles. Given the remarkable development and success of the latter [3], it is clearly very desirable to have a QMC method that can use exactly the same machinery and systematically include correlation effects by simply building stochastic ensembles of the independent particle solutions. Vigorous attempts have been made from several fields to explore this possibility [4, 5, 6, 7].

A significant hurdle exists, however: except for special cases (e.g., Hubbard), the two-body interactions will require auxiliary fields that are *complex*. As a result, the single-particle orbitals become complex, and the MC averaging over AF configurations becomes an integration over complex variables in many dimensions. A phase problem thus occurs which ultimately defeats the algebraic scaling of MC and makes the method scale exponentially. This is analogous to but more severe than the fermion sign problem with real AF [8, 9] or in real-space methods [10]. No satisfactory, general approach exists to control the phase problem. As a result, only small systems or special forms of interactions can be treated.

In this paper we address this problem. We develop a method for many-fermions that allows the use of any one-particle basis. It projects out the ground state by random walks in the space of Slater determinants. The phase problem is eliminated with an approximation that relies on a trial wave function $|\Psi_T\rangle$. We demonstrate the method by applying it to electronic systems using a plane-wave basis and non-local pseudopotentials, which can be implemented straightforwardly in this method. We calculate the binding energy of Si_2 and the cohesive energy of bulk Si using fcc supercells consisting of up to 54 atoms (216 electrons). These calculations represent the first application of AF-based QMC to solids. The results are in excellent agreement with experiments and are comparable to the best existing theoretical results. Particularly worth noting is that our results were obtained with a trial wave function which is a single Slater determinant formed by orbitals from density functional theory (DFT) calculations (with the local density approximation (LDA)), with no additional parameters or optimization.

The Hamiltonian for any many-fermion system with two-body interactions can be written in any one-particle basis in the general form

$$\hat{H} = \hat{H}_1 + \hat{H}_2 = \sum_{i,j}^{N} T_{ij} c_i^\dagger c_j + \frac{1}{2} \sum_{i,j,k,l}^{N} V_{ijkl} c_i^\dagger c_j^\dagger c_k c_l, \quad (1)$$

where N is the size of the chosen one-particle basis, and $c_i^\dagger$ and c_i are the corresponding creation and annihilation operators. Both the one-body (T_{ij}) and two-body matrix elements (V_{ijkl}) are known.

To obtain the ground state $|\Psi_G\rangle$ of $\hat{H}$, QMC methods use the imaginary time propagator $e^{-\tau\hat{H}}$ acting on a trial wave function $|\Psi_T\rangle$: $\lim_{n\to\infty}(e^{-\tau\hat{H}})^n |\Psi_T\rangle \propto |\Psi_G\rangle$. $|\Psi_T\rangle$ must not be orthogonal to $|\Psi_G\rangle$, and we will assume that it is of the form of a single Slater determinant or a linear

combination of Slater determinants. The time step τ is chosen to be small enough so that $\hat{H}_1$ and $\hat{H}_2$ in the propagator can be accurately separated with the Trotter decomposition.

The propagator $e^{-\tau \hat{H}_1}$ is the exponential of a one-body operator. A propagator of this form acting on a Slater determinant is straightforward to calculate, and it simply yields another determinant. The two-body propagator $e^{-\tau \hat{H}_2}$ can be expressed as an integral of propagators of this form, as follows. Any two-body operator can be written as a quadratic form of one-body operators: $\hat{H}_2 = -\frac{1}{2}\sum_\alpha \lambda_\alpha \hat{v}_\alpha^2$, where λ_α is a real number and $\hat{v}_\alpha$ is a one-body operator. The Hubbard-Stratonovich (HS) transformation [11] then allows us to write

$$e^{-\tau \hat{H}_2} = \prod_\alpha \left(\frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-\frac{1}{2}\sigma_\alpha^2}\, e^{\sqrt{\tau}\,\sigma_\alpha \sqrt{\lambda_\alpha}\,\hat{v}_\alpha}\, d\sigma_\alpha \right). \quad (2)$$

Introducing vector representations $\sigma \equiv \{\sigma_1, \sigma_2, \cdots\}$ and $\hat{\mathbf{v}} = \{\sqrt{\lambda_1}\,\hat{v}_1, \sqrt{\lambda_2}\,\hat{v}_2, \cdots\}$, we have the desired form

$$e^{-\tau \hat{H}} = \int P(\sigma)\, B(\sigma)\, d\sigma, \quad (3)$$

where $P(\sigma)$ is the normal distribution in Eq. (2) and

$$B(\sigma) \equiv e^{-\tau \hat{H}_1/2}\, e^{\sqrt{\tau}\sigma\cdot\hat{\mathbf{v}}}\, e^{-\tau \hat{H}_1/2} \quad (4)$$

is a one-body propagator.

The imaginary-time propagation thus requires evaluating the multidimensional integral in Eq. (3) over time slices n and the corresponding auxiliary fields. MC techniques are the only way to evaluate such integrals efficiently. We use a random walk approach [9]. In each step, a walker $|\phi\rangle$, which is a single Slater determinant, is propagated to a new position $|\phi'\rangle$: $|\phi'(\sigma)\rangle = B(\sigma)|\phi\rangle$, where σ is a random variable sampled from $P(\sigma)$. After a sufficient number of steps (iterations), the ensemble of random walkers is a MC representation of the ground-state wave function: $|\Psi_G\rangle \doteq \sum_{\phi'} |\phi'\rangle$.

In general λ_α cannot be made all positive in Eq. (2) [12]. The one-body operators $\hat{\mathbf{v}}$ are therefore complex. As the projection proceeds, the orbitals in the random walkers will become complex. As a result, the statistical fluctuations in the MC representation of $|\Psi_G\rangle$ increase exponentially with projection time $\beta \equiv n\tau$. This is the phase problem referred to earlier. It is of the same origin as the sign problem that occurs when $B(\sigma)$ is real. The phase problem is more severe, however, because for each $|\phi\rangle$, instead of a $+|\phi\rangle$ and $-|\phi\rangle$ symmetry [9], there is now an infinite set $\{e^{i\theta}|\phi\rangle\}$ ($\theta \in [0, 2\pi)$) from which the random walk cannot distinguish. At large β, the phase of each $|\phi\rangle$ becomes random, and the MC representation of $|\Psi_G\rangle$ becomes dominated by noise. This problem is generic, and the same analysis would apply if we had chosen, instead of the random walk, the standard AF QMC sampling approach [2]. In Fig. 1, the curves labeled "free projection" illustrate the phase problem.

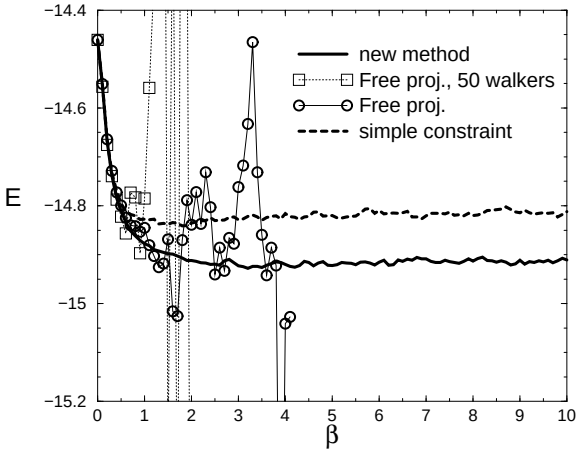

FIG. 1: Illustration of the phase problem and constraints to control it. The total valence energy (in Ry) of an fcc Si primitive cell (2 atoms) is shown as a function of projection time $\beta = n\tau$, with $\tau = 0.05$ Ry^{-1}. Unless otherwise indicated, 10,000 walkers are used. Increasing the number of walkers from 50 to 10,000 only slightly delays the onset of the phase problem. Simple generalization of the constraint that worked well for real determinants leads to poor results. The new method gives accurate results (note the agreement with the solid free projection curve, which is exact, until the latter becomes too noisy at $\beta \sim 1.5$).

Existing fixed-node type approximations have often worked very well to control the sign/phase problem in real space [13, 14] or in Slater determinant space when the propagator is real [9]. The phase problem here is unique because not only do the determinants acquire overall phases, but the internal structures of their orbitals become complex. The real-space analogy would be to have walkers whose coordinates become complex. This makes straightforward generalization of existing approaches ineffective. For example, similar to the constrained path approximation [9] we could impose the condition $\mathrm{Re}\langle\Psi_T|\phi\rangle > 0$. Or, in the spirit of the fixed-phase approximation in real space [14] we could project the walker by including a factor $\cos(\Delta\theta)$ in the weight, where $\Delta\theta$ is the phase of $\langle\Psi_T|\phi'\rangle/\langle\Psi_T|\phi\rangle$. They give similar results and do not work well [6]. The former is shown in Fig. 1 ("simple constraint"). Importance sampling with $\mathrm{Re}\langle\Psi_T|\phi\rangle$ or $|\langle\Psi_T|\phi\rangle|$ does not change the results [15].

To formulate a new method that can better separate the overall phase from the determinant, we first borrow from the idea of importance sampling [16], although our choice of the so-called importance function, $\langle\Psi_T|\phi\rangle$, is actually *complex*. We modify Eq. (3) to obtain the following new propagator for $|\phi\rangle$:

$$\int \langle\Psi_T|\phi'(\sigma-\bar{\sigma})\rangle\, P(\sigma-\bar{\sigma}) B(\sigma-\bar{\sigma}) \frac{1}{\langle\Psi_T|\phi\rangle}\, d\sigma, \quad (5)$$

where we have included a constant shift [5] $\bar{\sigma}$ in the integral in Eq. (3), which does not affect the equality. Eq. (5) can be re-written as

$$\int P(\sigma)\, W(\sigma,\phi)\, B(\sigma-\bar{\sigma})\, d\sigma, \tag{6}$$

where

$$W(\sigma,\phi) \equiv \frac{\langle\Psi_T|\phi'(\sigma-\bar{\sigma})\rangle}{\langle\Psi_T|\phi\rangle} e^{\sigma\cdot\bar{\sigma}-\frac{\bar{\sigma}\cdot\bar{\sigma}}{2}}. \tag{7}$$

The new propagator in Eq. (6) defines a new random walk. In each step the walker $|\phi\rangle$ is propagated to $|\phi'\rangle$ by $B(\sigma-\bar{\sigma})$: $|\phi'(\sigma-\bar{\sigma})\rangle = B(\sigma-\bar{\sigma})|\phi\rangle$, where σ is again sampled from $P(\sigma)$. $W(\sigma,\phi)$ is a c-number which can be accounted for by having every walker carry an overall weight factor and updating them according to: $w_{\phi'} = W(\sigma,\phi)w_\phi$. Formally the MC representation of $|\Psi_G\rangle$ in the new random walk is:

$$|\Psi_G\rangle \doteq \sum_{\phi'} w_{\phi'} \frac{|\phi'\rangle}{\langle\Psi_T|\phi'\rangle}. \tag{8}$$

For any choice of the shift $\bar{\sigma}$, the new random walk is an exact procedure to realize the imaginary time propagation, in the sense of Eq. (8). The optimal choice of $\bar{\sigma}$ is determined by minimizing the fluctuation of $W(\sigma,\phi)$ with respect to σ. To $\mathcal{O}(\sqrt{\tau})$ this yields

$$\bar{\sigma} = -\sqrt{\tau}\frac{\langle\Psi_T|\hat{\mathbf{v}}|\phi\rangle}{\langle\Psi_T|\phi\rangle}. \tag{9}$$

With this choice the leading σ-dependent term in W is reduced to $\mathcal{O}(\tau)$ and, by expanding $B(\sigma-\bar{\sigma})$ in $|\phi'\rangle$ in Eq. (7), we can manipulate W into the following form:

$$W(\sigma,\phi) \doteq \exp\left[-\tau\frac{\langle\Psi_T|\hat{H}|\phi\rangle}{\langle\Psi_T|\phi\rangle}\right] \equiv \exp[-\tau E_L(\phi)], \tag{10}$$

where the term E_L parallels the local energy in real-space QMC methods. Both E_L and the shift $\bar{\sigma}$ in Eq. (9) are independent of any overall phase factor of $|\phi\rangle$.

The weight of the walker in the new random walk is determined by E_L. In the limit of an exact $|\Psi_T\rangle$, E_L is a real constant, and the weight of each walker remains real. The so-called mixed estimate for the energy is phaseless:

$$E_G = \frac{\langle\Psi_T|\hat{H}|\Psi_G\rangle}{\langle\Psi_T|\Psi_G\rangle} \doteq \frac{\sum_{\phi'} w_{\phi'} E_L(\phi')}{\sum_{\phi'} w_{\phi'}}. \tag{11}$$

With a general $|\Psi_T\rangle$ which is not exact, a natural approximation is to replace E_L in Eq.'s (10) and (11) by its real part, $\mathrm{Re}E_L$. We have thus obtained a phaseless formalism for the random walk, with real and positive weights in Eq.'s (8) and (11).

Despite this, an additional constraint is still required. To illustrate the problem we consider the overlap $\langle\Psi_T|\phi'\rangle$ during the random walk. Let us denote the phase of $\langle\Psi_T|\phi'(\sigma-\bar{\sigma})\rangle/\langle\Psi_T|\phi\rangle$ by $\Delta\theta$, which is in general non-zero (of order $-\sigma\mathrm{Im}\bar{\sigma}$). This means that, the walkers will undergo a random walk in the complex plane defined by $\langle\Psi_T|\phi'\rangle$. At large β they will therefore populate the complex plane symmetrically, independent of their initial positions. It is useful to contrast the situation with the special case of a *real* $\hat{\mathbf{v}}$. For any $\hat{\mathbf{v}}$ the shift $\bar{\sigma}$ diverges as a walker approaches the origin in the complex plane, i.e., as $\langle\Psi_T|\phi'\rangle \to 0$. The effect of the divergence is to move the walker away from the origin. With a *real* $\hat{\mathbf{v}}$, $\Delta\theta = 0$ and the random walkers move only on the real axis. If they are initialized to have positive overlaps with $|\Psi_T\rangle$, $\bar{\sigma}$ will ensure that the overlaps remain positive throughout the random walk, much like in fixed-node diffusion Monte Carlo (DMC) in real space. Thus in this case the phaseless formalism reduces to the constrained path Monte Carlo method of Ref. [9], and it alone is sufficient to control the sign problem. For a *complex* $\hat{\mathbf{v}}$, however, the random walk is "rotationally invariant" in the complex plane, and the divergence of $\bar{\sigma}$ is not enough to prevent the build-up of a finite density at the origin. Near the origin the local energy E_L diverges, which causes diverging fluctuations in the weights of walkers. To address this we make an additional approximation. We project the random walk to "one-dimension" and multiply the weight of each walker in each step by $\max\{0,\cos(\Delta\theta)\}$. Imposing instead $\mathrm{Re}\langle\Psi_T|\phi'\rangle > 0$ gave similar results, but with somewhat larger variance.

We apply the new method to Si atom, molecule, and bulk. The Si^{4+} ions are represented by a norm-conserving LDA Kleinman-Bylander (KB) non-local pseudopotential [17]. We use periodic boundary conditions, and a plane-wave basis with a kinetic energy cut-off $E_{\mathrm{cut}} = 12.25$ Ry. The error resulting from E_{cut} was estimated through LDA calculations and is smaller than the MC statistical errors. The pseudopotential can be applied in essentially the same way as in plane-wave-based LDA calculations [15]. Calculations involving $\hat{\mathbf{v}}$ and the local part of the pseudopotential are efficiently handled using fast Fourier transforms. The separable KB form of the non-local pseudopotential makes its application as efficient as in LDA plane-wave codes. Our $|\Psi_T\rangle$ is a single Slater determinant consisting of LDA orbitals.

In Table I, we show results for the atom and molecule. Additional calculations with $a = 22a_B$ supercells show that finite-size errors at $a = 19a_B$ were smaller than the MC statistical errors. Our calculated Si_2 binding energy is in excellent agreement with the experimental value [18].

In the bulk calculations, we use fcc supercells consisting of 2, 16, 54 atoms (5209 plane waves). As Fig. 1 shows, the new method leads to a large improvement. Results for 16 and 54 atoms are shown in Table II. Our calculation for 54 atoms took several days on 20 Compaq Alpha 667 MHz processors. For the bulk cohesive energy, we first included a correction for the independent-particle finite-size error from the LDA results. We then corrected

TABLE I: Total valence energies of Si and Si_2, and binding energy of Si_2. The Si_2 ground state is $^3\Sigma_g^-$ (electronic configuration $5\uparrow\ 3\downarrow$). Calculations were done at the experimental equilibrium bond length of $4.244a_B$, in a cubic supercell with $a = 19a_B$ (4945 plane waves). Energies are in eV. Error bars are in the last digit and are in parentheses.

	Si	Si_2	Si_2 E_B
LDA	−102.648	−209.175	3.879
QMC	−103.45(2)	−210.03(7)	3.12(8)
Experiment			3.21(13)

TABLE II: Cohesive energy of bulk Si. Calculations are done for fcc supercells with 16 and 54 atoms, at $a_{\rm exp} = 5.43$Å. QMC result at ∞ is from 54 atoms and includes two finite-size corrections: (i) an independent-particle correction of 0.311 eV from LDA and (ii) an additional Couloumb correction of −0.174 eV from Ref. [20, 22]. A zero-point energy correction of −0.061 eV was also added to the calculated results at ∞. Energies are in eV per atom. Error bars are in the last digit and are in parentheses.

	16	54	∞
LDA	3.836	4.836	5.086
QMC	3.79(4)	4.51(3)	4.59(3)
Experiment			4.62(8)

for the remaining Couloumb finite-size error [19] using the results of Kent *et al.* [20]. Our result is again in excellent agreement with the experimental value (from Ref. [13]). It also compares very well with the result of a recent fixed-node DMC calculation [21], which also used a 54-atom supercell and gave 4.63(2) eV per atom after similar finite-size and zero-point energy corrections.

Without an exact solution to the sign/phase problem, reducing the reliance on trial wave functions is clearly of key importance to increasing the predictive power of QMC. For continuum electronic systems such as our test cases above, fixed-node DMC has often been the most accurate theoretical method [13]. It is encouraging that the new method, using simple LDA trial wave functions, gave comparable results to DMC. For similar supercells DMC often uses trial wave functions with 30-100 additional parameters [13]. Obtaining a good enough $|\Psi_T\rangle$ is instrumental to a successful DMC calculation, and often constitutes a substantial effort. The quality of $|\Psi_T\rangle$ controls the systematic errors from the fixed-node approximation and the variance. It also affects errors due to the locality approximation [23], which has been employed by most DMC calculations with non-local pseudopotentials. In the new method the latter approximation is eliminated. It remains to be seen whether the present method could lead to more accurate results than fixed-node DMC for continuum systems. This has been possible in some cases [24] with real AF in the Hubbard model.

We have presented a general framework. Various possibilities exist for further improvement of the method. An improved $|\Psi_T\rangle$ will give improved results. The freedom to choose the one-particle basis and the form of HS transformation, both of which can impact the quality of the results, offers significant opportunities. For periodic systems it should be possible to generalize the formalism to allow **k**-point sampling.

In conclusion, we have described a method for ground-state QMC calculations that allows the use of any one-particle basis. The method is general and applies to any Hamiltonian of the form in Eq. (1). It provides an approximate way to control the phase problem in all AF-based QMC methods, while allowing many of their advantages to be retained that lead to their applications spanning several areas. We have shown that the method gave accurate results for systems from an atom to a large supercell, using a simple trial wave function.

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[1] R. Blankenbecler, *et al.*, Phys. Rev. D **24**, 2278 (1981).
[2] G. Sugiyama and S. E. Koonin, Ann. Phys. (NY) **168**, 1 (1986).
[3] W. Kohn, Rev. Mod. Phys. **71**, 1253 (1999).
[4] P. L. Silvestrelli *et al.*, Phys. Rev. Lett. **71**, 1148 (1993).
[5] N. Rom *et al.*, Chem. Phys. Lett. **270**, 382 (1997).
[6] M. T. Wilson and B. L. Gyorffy, J. Phys. Condens. Matter **7**, 371 (1995).
[7] See, e.g., Y. Alhassid *et al.* Phys. Rev. Lett. **72**, 613 (1994); R. Baer and D. Neuhauser, J. Chem. Phys. **112**, 1679 (2000); C. W. Johnson and D. J. Dean, Phys. Rev. C **61** 044327 (2000); and references therein.
[8] E. Y. Loh Jr., *et al.*, Phys. Rev. B **41**, 9301 (1990).
[9] Shiwei Zhang *et al.*, Phys. Rev. B **55**, 7464 (1997).
[10] K. E. Schmidt and M. H. Kalos, in *Applications of the Monte Carlo Method in Statistical Physics*, ed. by K. Binder (Springer Verlag, Heidelberg, 1984).
[11] R. L. Stratonovich, Sov. Phys. Dokl. **2**, 416 (1958); J. Hubbard, Phys. Rev. Lett. **3**, 77 (1959).
[12] Shifting the potential can in principle make λ_α positive, but causes large fluctuations (see, e.g., Ref. [4]) and gives poor results when a constraint is used.
[13] W. M. C. Foulkes *et al.*, Rev. Mod. Phys. **73**, 33 (2001), and references therein.
[14] G. Ortiz *et al.*, Phys. Rev. Lett. **71**, 2777 (1993).
[15] Shiwei Zhang and H. Krakauer, unpublished.
[16] M.H. Kalos *et al.*, Phys. Rev. **A9**, 2178 (1974).
[17] A. M. Rappe *et al.*, Phys. Rev. B **41**, 1227 (1990).
[18] R. W. Schmude *et al.*, J. Chem. Phys. **99**, 7998 (1993).
[19] In Ref. [20], the DMC calculations used L-point sampling, but it was pointed out that, after the independent-

particle correction, the remaining Couloumb finite-size error is approximately the same for Γ-point sampling.
[20] P. R. C. Kent *et al.*, Phys. Rev. B **59**, 1917 (1999).
[21] W.-K. Leung *et al.*, Phys. Rev. Lett. **83**, 2351 (1999).
[22] P. R. C. Kent, private communication.
[23] L. Mitas *et al.*, J. Chem. Phys. **95**, 3467 (1991).
[24] Shiwei Zhang, cond-mat/9909090.